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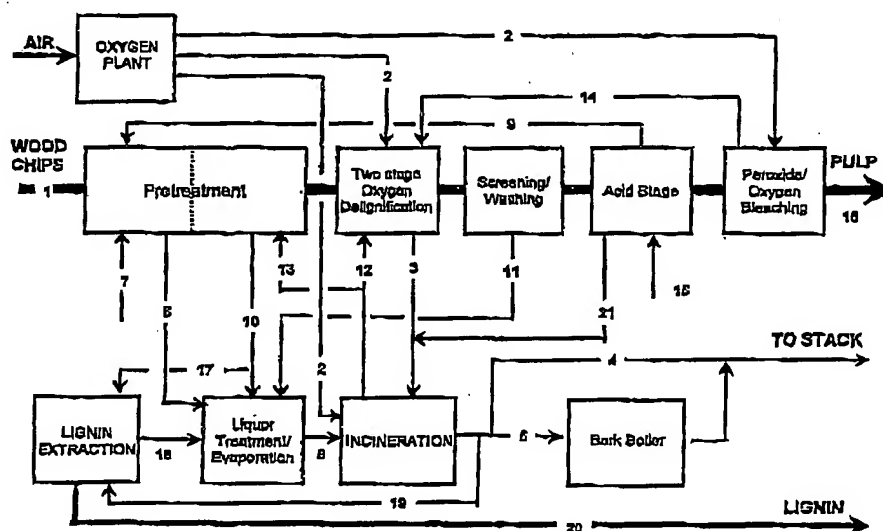
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(54) Title: PROCESS FOR OXYGEN PULPING OF LIGNOCELLULOSIC MATERIAL AND RECOVERY OF PULPING CHEMICALS



(57) Abstract

The process of the present invention relates to a substantially sulfur free process for the manufacturing of a chemical pulp with an integrated recovery system for recovery of pulping chemicals. The subject process is carried out in several stages involving physical and chemical treatment of lignocellulosic material in order to increase accessibility of the lignocellulosic material to reactions with an oxygen-based delignification agent. Spent cellulose liquor comprising lignin components and spent chemical reagents is fully or partially oxidized in a gas generator wherein a stream of hot raw gas and a stream of alkaline chemicals and chemical reagents is formed for subsequent recycle and reuse in the pulp manufacturing process.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL-TYPE SEARCH REPORT

(PCT Article 15.5)

National application No. 0202711-8	Country or Office of filing SE	Applicant's or agent's file reference MH/AN 48074
Filing date (day/month/year) 12 September 2002		(Earliest) Priority Date (day/month/year)
Applicant KIRAM AB		

Date of request for international-type search 30 October 2002	International-type search request No. SE 02/00973
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This international-type search report has been prepared by this International Searching Authority and is transmitted to the applicant.

This international-type search report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. ☐ Certain claims were found unsearchable (See Box I).
2. ☐ Unity of invention is lacking (See Box II).
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☐ filed with the international application.
☐ furnished by the applicant separately from the international application,

☐ but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.

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INTERNATIONAL-TYPE SEARCH REPORT

Search request No.

SE 02/00973

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: D21C 11/00, D21C 11/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 0047812 A1 (KIRAM AB), 17 August 2000 (17.08.00), page 14, line 1 - line 9; page 15, line 4 - line 14, claims 1,13, abstract --	1-13
X	US 4248662 A (SCOTT A. WALLICK), 3 February 1981 (03.02.81), column 3, line 6 - line 11, abstract --	1-13
A	US 6348128 A (HONGHI N. TRAN ET AL), 19 February 2002 (19.02.02), abstract -- -----	1-13

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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INTERNATIONAL-TYPE SEARCH REPORT

Information on patent family members

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SE 02/00973

WO	0047812	A1	17/08/00	AU	5889699	A	21/03/00
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				CA	2356444	A	17/08/00
				CN	1340121	T	13/03/02
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				SE	9900191	A	02/03/00
				WO	0012854	A	09/03/00

US	4248662	A	03/02/81	NONE
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				AU	4410399	A	20/12/99
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				CN	1307657	T	08/08/01
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				WO	9963151	A	09/12/99
				US	6501483	B	31/12/02

Autocausticizing alkali and its use in pulping and bleaching**

SUMMARY

Sodium salts of boric, phosphoric and silicic acids and sodium aluminates were found to be able to expel carbon dioxide from sodium carbonate during heating under certain conditions. The resulting smelts and ashes were strongly alkaline, and their water solutions were able to act satisfactorily as alkali during delignification of wood, thereby replacing sodium hydroxide in e.g. alkali cooking, oxygen-alkali cooking and bleaching and kraft cooking. Since the salts mentioned function essentially as hydroxide generators, the delignification will proceed largely in the same way as when sodium hydroxide is used, provided the composition of the salt is chosen properly, and the resultant pulps will be quite similar. Spent liquors from this kind of cooking or bleaching will, after appropriate burning and dissolution of the residue, give rise to liquors of the same kind as those used for the cooking and bleaching, respectively. This principle of alkali regeneration is termed autocauticizing. It renders unnecessary the conventional causticizing by lime of carbonate-containing smelt solutions, e.g. in kraft pulp mills. In this way the system of cooking chemicals in industrial alkaline pulping may be considerably simplified, which, in turn, will imply investment savings during building or renewal of pulp mills. Sodium borates seem to be the most promising of the compounds investigated, as

regards both pulping and regeneration. The results from the laboratory experiments indicate that losses of material via the flue gases will diminish when, in place of common hydroxide-carbonate-based liquors, spent liquors based on borates and phosphates are burnt in recovery furnaces. However, the results from the laboratory work call for trials on a technical scale, especially those of the burning of autocauticizable spent liquors.

TIVISTELMÄ

(Autokaustisoituvuutta emäs ja sen käyttö keittos- ja valkaisuksessa.)

Boori-, fosfori- ja piihapon natriumsuolat sekä natriumalumiinaatit havaittiin kykeneviksi korvaamaan hiilidioksidin natriumkarbonaattista lämmittäessään määrättyissä oloissa. Muodostuneet sulat ja tuhkat olivat vahvasti emäksisiä ja niiden vesiliuokset pystyivät toimimaan tyydyttävästi alkalina puun delignifioinnissa korvaten täällöin natriumhydroksidin esim. alkalikeitossa, happi-alkalikeitossa ja -valkaisuksessa sekä sulfaattikeitossa. Koska mainitut suolat toimivat pitkäaikaan hydroksidilähteinä, delignifiointi tapahtuu suurelta osin samoin kuin käytettäessä hydroksidia, edellyttäen, että suolan koostumus valitaan sopivasti, ja saatavat massat ovat siten samanlaisia. Tällaisen keiton tai

valkaisuksen jäte-liuoksista saadaan sopivan polton ja jäätännöksen luovutuksen jälkeen samanlaisia liuoksia kuin ne, joita keitossa ja valkaisuksessa käytettiin. Tässä emäksen kalteenotto-omaisuutta nimitetään autokaustisoinniksi. Se tekee tarpeettomaksi normaalin karbonaattia sisältävien suolaliuosten kaustisoinnin kalkin avulla, esim. sulfaattitehtailla. Tällä tavoin teollisessa mittassa tapahtuvan alkalisen keiton keittokemikaalijärjestelmää voidaan yksinkertaistaa huomattavasti, mikä puolestaan merkitsee investointisäästöjä rakennuttaessa tai uudistettaessa massatehtaita. Natriumboraa- tai -natriumfosfaattiliuoksista tällaisista yhdisteistä sekä keiton että regeneroinnin suhteen. Laboratoriotulokset viittaavat siihen, että savukaasujen mukana tapahtuvat materiaalihäviöt vähenevät, kun tavallisen hydroksidikarbonaattipohjaisen lipeän sijasta soodakattilassa poltetaan boraatti- ja fosfaattipohjaisia jäteliuoksia. Kuutenkin laboratoriotutkimuksen tulokset vaativat koeajoja teknisessä mittassa, erityisesti autokaustisoituvien jäteliuosten polttokokeita.

* Jan Janson, Lic.Sc., Pulping Department, Oy Keskuslaboratorio — Centrallaboratorium Ab (The Finnish Pulp and Paper Research Institute), P.O. Box 136, SF-00101 Helsinki 10, Finland.

** Inaugural dissertation.

LIST OF PUBLICATIONS

This thesis is based on the following papers referred to in the text by the Roman numerals I—VI, and on some new results not published earlier.

- I. Janson, J.: The use of unconventional alkali in cooking and bleaching. Part 1. A new approach to liquor generation and alkalinity. Paperi ja Puu — Papper o. Trä 59 (1977): 6—7, 425—430.
- II. Janson, J. and Pekkala, O.: The use of unconventional alkali in cooking and bleaching. Part 2. Alkali cooking of wood

with the use of borate. Paperi ja Puu — Papper o. Trä 59 (1977): 9, 546—548, 551—552, 555—557.

- III. Janson, J. and Pekkala, O.: The use of unconventional alkali in cooking and bleaching. Part 3. Oxygen-alkali cooking and bleaching with the use of borate. Paperi ja Puu — Papper o. Trä 60 (1978): 2, 89—93.
- IV. Janson, J.: The use of unconventional alkali in cooking and bleaching. Part 4. Kraft cooking with the use of borate. Paperi ja Puu — Papper o. Trä 60 (1978): 5,

349—352, 355—357.

- V. Janson, J.: The use of unconventional alkali in cooking and bleaching. Part 5. Autocausticizing reactions. Paperi ja Puu — Papper o. Trä 61 (1979): 1, 20—24, 27—30.
- VI. Janson, J.: The use of unconventional alkali in cooking and bleaching. Part 6. Autocausticizing of sulphur-containing model mixtures and spent liquors. Paperi ja Puu — Papper o. Trä 61 (1979): 2, 98—103.

The effect of borates on kraft, kraft-AQ and soda-AQ cooking of black spruce

Keywords

*Kraft pulping,
alkaline pulping,
anthraquinone,
sodium borate,
causticizing,
yield,
Picea mariana.*

ABSTRACT

The effects of disodium borate, an autocauticizing agent, on alkali requirement, cooking time, pulp yield, and pulp quality were studied by pulping black spruce chips in kraft, kraft-AQ and soda-AQ processes. Borates were found to retard delignification of black spruce in all three processes. The retardation of kraft pulping can be compensated by adding anthraquinone, increasing the alkali charge, extending the cooking time, and increasing the cooking temperature. Since the yield and quality of the kraft pulps were unaffected by borates, they can be considered for implementation in kraft mills. If the recovery process is found to be economically and commercially feasible. Borates were unattractive for sulphur-free soda-AQ pulping of black spruce, making this process extremely slow and resulting in poor yield and pulp quality.

TIIVISTELMÄ

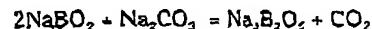
Natriumboraatin vaikutukset mustakuusen sulfaatti-, sulfaatti-antrakinoni- ja sooda-antrakinonikeitossa

Natriumboraatin vaikutuksia alkalinkulutukseen, keittoaikaan, massan saantoon ja massan laatuun selvitettiin mustakuusen sulfaatti-, sulfaatti-antrakinoni- ja sooda-antrakinonikeitoissa. Boraatin havaittiin hidastavan delignifiointia kaikissa prosesseissa. Sulfaattikeitossa hidastuminen voidaan kompensoida lisäämällä antrakinonia ja/tai alkaliannosta, pidentämällä keittoaikaa ja/tai nostamalla keittolämpötilaa. Koska boraatilla ei ollut vaikutuksia massan saantoon eikä laatuun, sen käyttöä sulfaattitehtaalissa voi harkita mikäli talteenotto-prosessi osoitautuu taloudellisesti ja kaupallisesti järkeväksi. Boraatit eivät sovi mustakuusen rikittömään sooda-antrakinonikeittoon, koska ne tekevät tämän prosessin äärimmäisen hitaaksi ja tuloksena on huonolaatuinen ja -saantoinen massa.

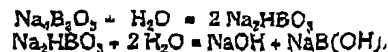
^{1,2,3} Susanne Prihoda, Paweł Wandelt, George J. Kubes, Pulp and Paper Research Institute of Canada and Department of Chemical Engineering, Pulp and Paper Research Centre, McGill University 3420, University Street, Montreal, Canada, H3A 2A7.
³ Present address: Institute of Papermaking and Paper Machines, Technical University of Łódź, ul. Wolczanska 219/223, 93-005 Łódź, Poland.

INTRODUCTION

High capital and operating costs of the chemical recovery system in kraft mills generate interest in its simplification. One way to achieve this goal is to eliminate the recausticizing and lime kiln operations by using autocauticizable cooking chemicals. Such an autocauticizing process was developed in Finland by Janson /1-8/ in the seventies. The process involves disodium borate, Na_2HBO_3 , as a source of effective alkali replacing sodium hydroxide. The disodium borate is converted to monosodium borate during cooking. In the recovery furnace, the monosodium borate is dehydrated to sodium metaborate, NaBO_2 , and organic sodium salts are converted, as in the conventional system, to sodium carbonate. Sodium metaborate reacts with sodium carbonate in the recovery furnace to produce carbon dioxide and tetrasodium diborate:



White liquor can be obtained simply by hydrolysing the tetrasodium diborate according to the following chemical reactions:



Prospects for the implementation of the borate autocauticizing process depend on its competitiveness with the well-established conventional kraft process. A key criterion is whether the borate-based